

# MECHANISM OF VEGETABLE TANNAGE\*

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## ABSTRACT

The shrinkage temperature, linear shrinkage, and linear recovery in water of collagen fibers treated with catechin, polymerized catechin, wattle, and quinone at pH 3 and pH 4.5, and the change in the shrinkage temperature of variously treated fibers on using pure glycol or glycerol, in place of water, were studied. The results showed that, while the shrinkage behavior and characteristics of collagen tanned at pH 3 or pH 4.5 with wattle and polymerized catechin were similar, the shrinkage behavior of fibers tanned with quinone at pH 3 was different from that of fibers tanned with wattle. Fibers tanned with quinone at pH 4.5 exhibited a fairly appreciable linear recovery, but wattle- or polymerized catechin-tanned fibers did not recover. Also  $T_s$  of collagen fibers tanned at pH 4.5 with wattle or polymerized catechin, was drastically decreased whereas that of collagen fibers tanned similarly with quinone was enormously increased on using pure glycol, instead of water, as heating medium. These results showed that the mechanisms of vegetable and quinone tannage are not similar as far as shrinkage is concerned. Since quinone tannage in a neutral and fairly acidic medium is due to covalent forces, it can be said that the vegetable tannage involves forces other than the covalent ones.



## INTRODUCTION

It is well known that vegetable-tanned leather has good hydrothermal stability. But two basically different views have been expressed as to the cause of the good hydrothermal stability of vegetable-tanned leather. One view is that vegetable tannage involves noncovalent forces and the other is that it involves covalent forces. Recently, Endres and others (1-4) supported the view that the higher hydrothermal stability of vegetable-tanned leather is due to fixation of tannins by strong covalent forces while Shuttleworth and his co-workers (5-9) during the past few years have reiterated their support of the view that the higher hydrothermal stability of vegetable-tanned leather is due to fixation of tannins by

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weaker noncovalent forces. It should be stated that the supporters of the "covalent forces" theory do not preclude the existence of noncovalently bound material, but they are of the opinion that the higher hydrothermal stability of vegetable-tanned leather is due to covalently fixed material.

Endres' support of the "covalent fixation" theory (1, 2) is based on his observation that the  $T_s$  of reconstituted collagen, treated first at pH 4.5 with a vegetable tannin phenolic monomer like catechin, which is then oxidized and polymerized *in situ* by treatment with potassium ferricyanide, a mild oxidizing agent, is higher than the  $T_s$  of collagen treated at the same pH with externally oxidized and polymerized catechin. In view of the possibilities of the formation of quinone as an intermediary during oxidation and polymerization of catechin (10, 11), he considered that the greater rise in  $T_s$  of the former can be attributed to the quinone-like fixation of the intermediary products, since quinones like *p*-benzoquinone crosslink collagen by strong covalent forces at pH 4.5.

While it is possible that, during the polymerization of catechin-like vegetable tannin monomers, the corresponding quinone might be an intermediate (10, 11), it might not be present in tanning materials like wattle to take part in the covalent fixation. This was substantiated by the observation of Kedlaya and Basu (12) that the birefringence characteristics of vegetable- and quinone-tanned collagen fibers tanned at pH 4.0 to 4.5 were not similar to those of collagen fibers subjected to treatments with lyotropic agents like phenol. Shuttleworth and his colleagues (6-9) gave a large number of results in favor of the theory of fixation by noncovalent forces. One of these was the fact that, if pelt is treated with *p*-benzoquinone at pH 3, its  $T_s$  is not raised, whereas treatment with wattle at that pH raises the  $T_s$ . Hence an experiment was conceived that, in essence, combines the experimental technique of Endres (12) and that of Shuttleworth (6-7). Just as in the experiment of Endres, collagen fibers were treated in three ways: (a) with vegetable tannin monomer as such, (b) with vegetable tannin monomer under oxidative conditions, and (c) with *p*-benzoquinone; however, in all the treatments the pH of the infusion was maintained at pH 3, as was done by Shuttleworth. Shrinkage temperatures ( $T_s$ ) of the treated fibers were determined after washing the fibers well in (a) water at neutral pH, and (b) pure glycol or glycerol. In addition to  $T_s$ , percent change in the length of the fibers on shrinkage, that is, linear shrinkage (LS), and the percent recovery of the shrunken fiber on cooling (LR) were also determined in the case of shrinkage measurements in water. For comparative purposes, collagen fibers were also treated with wattle tannin at pH 3 and pH 4.5, and with *p*-benzoquinone at pH 4.5, and the tanned fibers were used in shrinkage measurements.

## EXPERIMENTAL

Collagen fibers, teased out of the tail of a just sacrificed one-year-old male albino rat, were washed well with water and transferred to a lime suspension for over-

night liming treatment. On the next day, the fibers were washed well and delimed with one percent ammonium sulfate solution in an infinite float. Delimed collagen fibers were treated with catechin, *p*-benzoquinone, or wattle under various conditions specified below. During the treatment, a mild agitation was maintained and a small piece of delimed pelt was added to the treatment bath to avoid preferential fixation of the material of the bath on the fibers being treated. The pH of the bath, wherever necessary, was adjusted to the required level with 0.1 N NaOH. An infinite float was maintained throughout the treatment.

The treatments given were:

1. Overnight with saturated catechin infusion at pH 4.5,
2. Six hours with saturated catechin infusion, and then overnight with one percent potassium ferricyanide (in order to carry out *in situ* oxidation of incorporated catechin),
3. Overnight at pH 4.5 and at pH 3 with an infusion of polymerized catechin obtained by treating saturated catechin infusion with one percent potassium ferricyanide,
4. Overnight with purified wattle extract at pH 3 and at pH 4.5 (for purification of the wattle, see below),
5. Overnight with saturated *p*-benzoquinone solution at pH 3, 4.5, and 6.5.

#### Purification of Wattle

A ten percent solution (100 ml.) of wattle extract was treated with an excess of ten percent solution of lead acetate in order to precipitate completely the phenolic constituents of wattle. Polyphenolic constituents of the precipitate were liberated by treating the thoroughly washed precipitate with a suitable ion exchange resin (Amberlite IR-120).

#### Shrinkage measurements

A modified version of the micro-shrinkage measurement technique developed by Nutting (13) was used in this work. The modification was required for carrying out linear shrinkage measurements. The apparatus was described in an earlier publication (14); the modes of measurement and calculation of linear shrinkage and recovery have also been given in that publication in detail. The image of a small piece of collagen fiber bundle, placed in two drops of heating fluid (water, glycol, or glycerol in the present work) on a cavity slide on a micro-hotplate, was projected on the screen of a projection microscope. The shrinkage temperature, and the lengths of the image of the fiber before shrinkage, after complete shrinkage, and after overnight recovery in the heating medium, were measured. From the dimensional shrinkage measurements, the percent linear shrinkage and recovery with reference to a particular heating medium were calculated.

In the present work,  $T_s$  values of variously treated collagen fiber bundles, in water, glycol, and glycerol, and LS and LR values of samples shrunk and recovered in water were determined. Fifty determinations of LS and LR values were carried out for statistical evaluation of the values.

## RESULTS AND DISCUSSION

From the shrinkage values in water of variously treated collagen fibers given in Table I, it is seen that, on treating delimed collagen fibers with catechin infusion at pH 4.5, the  $T_s$  increased by only 4°C. On treating the catechin-treated fiber with the mild oxidizing agent potassium ferricyanide the  $T_s$  increased by 22°C. The  $T_s$  of the collagen fiber also increased by 19°C. on treatment at pH 4.5 with preoxidized polymerized catechin liquor. The  $T_s$  of collagen fibers, tanned in wattle or quinone liquor at pH 4.5, in water, increased to a great extent. It is to be noted that there is a small difference of 3°C. in the  $T_s$  values of collagen fibers treated with externally polymerized catechin (pH 4.5) and of collagen fibers treated first with catechin at pH 4.5, and then oxidized internally, i.e., *in situ*. A similar difference was reported by Endres (1, 2). This difference might be the result of a uniform distribution of tannins and not of quinone-like fixation, as envisaged by Endres. The following results substantiate this viewpoint.

TABLE I  
SHRINKAGE BEHAVIOR IN WATER OF WATTLE-, CATECHIN-,  
AND QUINONE-TREATED COLLAGEN FIBERS

Sample No.	Treatment	pH of Treatment	$T_s$ (°C.)	LS (%)	LR (%)
1	Delimed	6.0	56	75 ± 5	10 ± 4
		3.0	Gelatinization		
2	Catechin	4.5	60	78 ± 7	8 ± 2
3	Catechin first and then $K_3Fe(CN)_6$	4.5	78	76 ± 6	< 2
4	Catechin treated with $K_3Fe(CN)_6$ prior to use in tanning	4.5	75	72 ± 7	< 2
		3.0	72	70 ± 9	< 2
5	Wattle (purified)	4.5	82	80 ± 8	< 2
		3.0	78	78 ± 8	< 2
6	Quinone	4.5	76	69 ± 8	33 ± 6
		3.0	Gelatinization		
		6.5	82	75 ± 7	44 ± 4

Dimensional shrinkage values (LS and LR) in water of collagen fibers treated in various ways at pH 4.5, given in Table I, show that there is no significant

difference in the LS values, but LR values of quinone-treated and wattle- or catechin-tanned (treated by either method described earlier) at pH 4.5 are not similar. While collagen fibers treated with wattle or with polymerized catechin (polymerized by either method) exhibited only very poor recovery, the fiber treated with *p*-benzoquinone at pH 4.5 exhibited recovery of  $33 \pm 6$  percent. Raw (delimed) collagen fibers and collagen fibers treated with catechin monomer alone at pH 4.5 exhibited a similar poor recovery. On treating collagen fibers with externally polymerized catechin or wattle at pH 3, there is good tanning action and the shrinkage behavior in water of collagen fiber thus treated is almost the same as that at pH 4.5, though there is a slight reduction in the values. While the fibers treated with quinone at pH 4.5 exhibited a good rise in  $T_s$  and an increase in LR, the fibers treated with quinone at pH 3 were gelatinized just like raw collagen kept in water at pH 3. If quinone tanning is done at pH 6.5, the pH at which quinone is assumed to fix maximally to collagen, the rise in  $T_s$  and increase in LR of collagen are quite appreciable.

It may be mentioned in this connection that Shuttleworth (6, 7) reported that the  $T_s$  of delimed skin pieces treated with the quinone at pH 3 was the same as that of delimed skin, whereas in this work collagen fibers treated with quinone were gelatinized. Absence of gelatinization or swelling in the former case is due to the salts added to suppress swelling. On adding three percent salt to the quinone solution at pH 3, gelatinization of collagen fibers was prevented and the  $T_s$  of fibers treated with the quinone solution containing salt and that of delimed collagen kept in salt solution (three percent) at pH 3 were the same, *viz.*, 50°C. The  $T_s$  of collagen fibers treated with wattle at pH 3 in the presence of salt (three percent) was found to be about 2°C. higher than that obtained in the absence of salt.

Results given in Table II on shrinkage of collagen fibers treated with *p*-benzoquinone and wattle or catechin polymer (polymerized by either method) at pH 4.5

TABLE II  
SHRINKAGE TEMPERATURE IN °C. IN VARIOUS HEATING MEDIA

Sample No.	Treatment	pH of Treatment	Water	Ethylene Glycol	Glycerol
1	Delimed	6.0-7.0	57	85	90
2	Catechin (polymerized <i>in situ</i> )	4.5	78	63	73
3	Catechin (externally polymerized)	4.5	75	62	74
		3.0	72	60	76
4	Wattle	4.5	82	62	74
		3.0	78	60	75
5	Quinone	4.5	76	86	92
		6.5	82	92	94

in pure nonaqueous solvents (ethylene glycol or glycerol), indicated their different behavior.

On using pure ethylene glycol or glycerol as the heating medium instead of water, the  $T_s$  of collagen fibers treated with wattle or polymerized catechin at pH 3 or 4.5 is considerably reduced, whereas the  $T_s$  of the *p*-benzoquinone-tanned fiber, tanned at pH 4.5, is considerably increased.

These results definitely indicate the basic difference in the mechanism of fixation of vegetable tannins similar to wattle and quinone in acidic medium as far as shrinkage characteristics are concerned.

Similarly, the  $T_s$ , LS, and LR characteristics of collagen fibers treated with wattle and polymerized catechin (polymerized by either method) at different pH values in water indicated the possibility of catechin and like tannin monomers present in the tan liquors being polymerized and taking part in tanning, and both wattle and polymerized catechins or like substances may tan by the same mechanism.

Quinone does not fix covalently to collagen at pH 3. Therefore the rise in  $T_s$  in water of collagen fibers on tanning with wattle or polymerized catechin (polymerized by either method) at pH 3 is not due to quinone-like fixation of vegetable tannins. Further, covalent crosslinks make the shrunken fiber recover well or fairly well, provided the fiber has not attained hydrophobicity to a fairly good extent, such as occurs in chrome tanning (16). This is the reason for the better LR values in water of collagen tanned with quinone at pH 4.5 or 6.5. Obviously, in the absence of such links, LR in water will be poor. This explains the poor LR of collagen fibers tanned with wattle or polymerized catechin (polymerized by either method).

The lowering of the  $T_s$  in glycol or glycerol medium of collagen fibers treated with wattle or polymerized catechin at pH 3 or 4.5 may perhaps be the result of the following: the affinity of polyphenols for glycol or glycerol may be greater than their affinities for collagen. As a consequence, the ability of glycol or glycerol to remove water from collagen is reduced. It is to be noted that Milch (17) is of the view that the higher  $T_s$  of raw collagen in ethylene glycol and such solvents is due to increased lateral order or "crystallinity" in the fiber caused by the solvent. The rise in  $T_s$  of the quinone-tanned fiber in pure glycol may also be due to this.

Endres *et al.* (8) also stated that the mechanism of vegetable tannage is similar to that of methyl quinone. But there was no rise in  $T_s$  in water of collagen fiber treated at pH 3 overnight with methyl quinone infusion aged for 24 or 48 hours. Actually, the fibers were gelatinized. The  $T_s$  in water of collagen fiber treated with methyl quinone at pH 3 in the presence of three percent salt is the same as that of raw or delimed collagen. This observation shows that the mechanisms of tanning of methyl quinone and wattle are different.

From the foregoing it may be inferred that vegetable tannins similar to wattle and quinone do not tan collagen by similar mechanisms under the pH conditions normally adopted in vegetable tannage. Since it is well established that quinone tannage at slightly acidic pH (4.5–6.5) involves a covalent type of fixation, it can be said that vegetable tannins do not fix covalently to collagen. Only forces other than covalent bonds such as hydrogen bonds are responsible for the higher hydrothermal stability of vegetable-tanned leathers. These results are in line with the views of Shuttleworth (6, 7).

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#### REFERENCES

1. Endres, H. *Das Leder*, **12**, 294 (1961).
2. Stadler, P., and Endres, H. *Das Leder*, **14**, 175 (1963).
3. Gustavson, K. H. *J. Soc. Leather Trades' Chemists*, **50**, 144, 445 (1966).
4. Endres, H., El Sissi, A. A., Ishak, M. S., and Steinburg, A. V. *Das Leder*, **16**, 174 (1965).
5. Shuttleworth, S. G. *J. Soc. Leather Trades' Chemists*, **50**, 252 (1966).
6. Shuttleworth, S. G. *J. Soc. Leather Trades' Chemists*, **51**, 134 (1967).
7. Russell, A. E., Shuttleworth, S. G., and Williams-Wynn, D. A. *J. Soc. Leather Trades' Chemists*, **51**, 222, 349 (1967).
8. Russell, A. E., Shuttleworth, S. G., and Williams-Wynn, D. A. *J. Soc. Leather Trades' Chemists*, **52**, 220 (1968).
9. Shuttleworth, S. G., Russell, A. E., and Williams-Wynn, D. A. *J. Soc. Leather Trades' Chemists*, **52**, 486 (1968).
10. Hathway, D. E., and Seakins, J. W. *J. Chem. Soc.*, 1562 (1957).
11. Hathway, D. E., and Seakins, J. W. *Biochem. J.*, **67**, 239 (1957).
12. Kedlaya, K. J., and Basu, B. C. *Leather Sci.*, **12**, 41 (1965).
13. Borasky, R., and Nutting, G. C. *JALCA*, **44**, 830 (1949).
14. Kedlaya, K. J., Ramanathan, N., and Nayudamma, Y. *Leather Sci.*, **15**, 40 (1968).
15. Mandelkern, L. "Annual Review of Physical Chemistry," Vol. 15, p. 42, Cornell University Press, Ithaca, N. Y., 1964.
16. Kedlaya, K. J. Ph.D. Thesis, University of Madras (1969).
17. Milch, R. A. *Biorheology*, **3**, 97 (1966).
18. Endres, H., Stadler, P., and El Sissi, A. A. *Das Leder*, **15**, 102 (1964).

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